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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

FERROUS IODIDE.

BY C. LORING JACKSON AND I. H. DERBY.

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THE accounts of anhydrous ferrous iodide which we have been able to find in the chemical literature are very contradictory. Serullas * seems to have been the first to obtain it by the rather strange method of passing iodine and steam through a red-hot iron tube filled with charcoal. He describes it as shining yellow crystals looking like gold filings. Gay Lussac and Davy * say it is a brown mass which fuses at a red heat and sublimes at a higher temperature. A. T. Thomson † treated one part of iron with two of iodine suspended in water, and after evaporating off the water in a flask containing some free iron, obtained a steel gray laminated mass melting at 177° and possessing a sharp puckery taste. When heated in air it left a residue of ferric oxide. In 1861 Carius and Wanklyn ‡ prepared it as a gray laminated mass by heating iron filings and iodine in a porcelain crucible. In 1863 De Luca § states that Faville had made it under his direction, and that it is a pure white amorphous powder. He gives no statement of the method of preparation in any of the journals which are accessible to us. Finally Erdmann || in his Lehrbuch (1898) describes it as a reddish brown body, also without giving the method of preparation. The color of ferrous iodide, therefore, is not by any means settled, the balance of evidence in the chemical literature being in favor of gray or white; but as no analyses of the anhydrous salt have been published, so far as we can find, none of the statements quoted above can be considered to rest on a solid foundation. Under

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* Gmelin-Kraut, Handbuch, III. 350, 6th edition.

† Pharmaceut. Journ., I. 44 (1842).

‡ Ann. Chem., CXX. 69.

§ Comptes-Rendus, LV. 615.

|| Lehrbuch der anorganischen Chemie, 62.

these circumstances it seemed worth while to take up the study of the ferrous iodide, and the results of our work in this field are contained in the following paper.

Preparation of Ferrous Iodide.

The method adopted consisted in passing the vapor of iodine over heated iron. In the first experiments a combustion tube was used with a stream of carbonic dioxide to carry the iodine, but as we found a temperature above the softening point of hard glass was necessary, we replaced the glass tube with one of iron, which we heated with a Fletcher's tube furnace. At the high temperature thus obtained the iron was oxidized by the carbonic dioxide, and the film of oxide thus formed protected the metal from the action of the iodine; accordingly the carbonic dioxide was replaced by nitrogen, after which good results were obtained.

The apparatus in its final form consisted of two large bottles, which served as gas holders for the nitrogen, and were united by glass tubes and rubber connectors in such a way that, by letting in water from the water works, the gas could be forced out of one of them at a regulated rate through the purifiers and the iron tube to the other bottle, in which it was collected. When this was full of gas, by a simple rearrangement of the pinch-cocks the nitrogen could be forced back through the apparatus again in the same direction as before into the first bottle. By means of this device the same nitrogen could be used over and over again, thus causing a great saving in time and labor. The nitrogen was made by the excellent method of Dr. Gibbs,* — equal parts of sodic nitrite, ammonic nitrate, and potassic dichromate were pulverized, and mixed with three parts of water in a flask with a wide delivery tube. The gas came off when the mixture was gently warmed. Twenty-four grams of the mixture gave about 1200 cc. of nitrogen. The nitrogen, after leaving the gas holder, was purified by passing through a solution of sodic hydrate, sulphuric acid, and a long column of calcic chloride, after which the oxygen was removed by means of a layer of finely divided copper heated in a tube of hard glass by means of a kerosene stove. This precaution was necessary, as the nitrogen was contaminated with air introduced when the tubes were opened, or from the water in the gas holders. We tried at first an alkaline solution of pyrogallol for the removal of the oxygen, but as we found this was not efficient, we resorted to the layer of finely divided copper, which was prepared by reducing cupric oxide.

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* Ber. d. chem. Ges., 1877, p. 1387.

The reaction took place in three steel bicycle tubes, the largest of which was one inch (2.54 cm.) in outside diameter and about one sixteenth of an inch (1.59 mm.) thick. The other tubes were somewhat thinner and small enough to slip tightly into the larger tube. The larger tube contained the iron, which was used in the form of wire clippings (card teeth), as it was found by experiment that these gave a better yield of iodide than turnings, filings, or iron by hydrogen. The iron was freed from organic matter by heating it in a stream of hydrogen before using it. The layer of iron in the tube was about 23 cm. long, and this portion of the tube was heated directly by the Fletcher furnace to a bright red heat. One of the smaller tubes was slipped into the larger one at its end nearest the gas holder containing the nitrogen, in this was placed the iodine, which was slowly volatilized by the heat conducted along the iron tube, and the vapor thus formed was swept over the hot iron in the furnace by the stream of nitrogen; this tube was connected with the purifiers by a perforated cork and glass tube far enough from the heat to avoid danger of burning. It was found wise to protect this cork from the iodine vapor, some of which crept back even against the current, by an asbestos or iron diaphragm. The second smaller iron tube was slipped into the further end of the larger tube, and reached the heated portion of it, so that the vapor of ferrous iodide formed in the larger tube condensed in the smaller one, from which it could be easily collected by withdrawing this smaller tube after it had cooled in the atmosphere of nitrogen. The joints of the iron tubes were rendered air tight by means of large rubber connectors, which were kept cool by winding them with lampwicking that dipped into a beaker of water. The receiving tube just described was connected with some bottles of strong sulphuric acid to prevent the creeping back of any aqueous vapor into the tube. The delivery tube from these bottles conveyed the nitrogen to one of the gas holders already described.

In carrying on the process it was observed that a considerable amount of iodine was taken up by the iron before any iodide distilled over; but after it began to appear, it continued to collect for several hours, so that the yield was a good one, and when the apparatus has been once set up the ferrous iodide can be obtained in quantity with little trouble.

As the product of the reaction just described had a deep red color in thin plates, and looked almost black when the mass was even moderately thick, we supposed at first that it could not be a ferrous salt, and accordingly applied the following tests. A little of it treated with water, in which it dissolved completely and with great ease, gave no color with a solution of potassic sulphocyanate, but a strong test for a ferrous salt with potassic ferricyanide. As it was possible that it might be a ferric iodide which was decomposed by water into the ferrous salt and free iodine, we next tested for iodine both with starch paste and with carbonic disulphide, but with negative results. These qualitative experiments indicated that the substance, in spite of its red color, was ferrous iodide; and that this is the case was proved by the following analyses. The substances used in I.–V. and in IX. and X. were the direct product of the reaction. In VI., VII., and VIII. this product had been purified by sublimation before it was analyzed.

I. 0.6717 gram of substance gave 1.0202 gram of argentic iodide and 0.1720 gram of oxide of iron.
II. 1.0400 gram of substance gave 1.5736 gram of argentic iodide.
III. 0.9658 gram of substance gave 1.4601 gram of argentic iodide.
IV. 0.7493 gram of substance gave 1.1471 gram of argentic iodide and 0.1934 gram of ferric oxide.
V. 0.8327 gram of substance gave 1.2586 gram of argentic iodide and 0.2209 gram of ferric oxide.
VI. 1.2675 gram of substance gave 1.9232 gram of argentic iodide and 0.3261 gram of ferric oxide.
VII. 0.7396 gram of substance gave 1.1192 gram of argentic iodide and 0.1932 gram of ferric oxide.
VIII. 0.5944 gram of substance gave 0.8978 gram of argentic iodide.
IX. 0.3831 gram of substance gave by ignition 0.0982 gram of ferric oxide.
X. 1.7526 gram of substance gave by ignition 0.4658 gram of ferric oxide.

		Percentages.	
		Iodine.	Iron.
Calculated for FeI_2		81.92	18.08
Found	I.	82.10	17.92
	II.	81.77	
	III.	81.74	
	IV.	82.71	18.07
	V.	81.66	18.56
	VI.	82.00	18.01
	VII.	81.76	18.28
	VIII.	81.64	
	IX.		17-94
	X.		18.60

Of these analyses I.–VIII. were made by passing sulphurous anhydride into the aqueous solution to convert any free iodine (formed by the action of air on the solution) into hydriodic acid, and to dissolve the ferric hydrate, if any, formed at the same time as the free iodine; then, after driving off the excess of the sulphurous anhydride, the iodine was precipitated as argentic iodide and the iron as ferric hydrate in the usual way. Analyses IX. and X. were made by simple ignition of the ferrous iodide in a porcelain crucible, when it loses all its iodine and is converted into ferric oxide.

Properties of Ferrous Iodide.

The anhydrous salt prepared as described above forms plates of a deep full red color with a slight brownish tint. This color is a much more pronounced red than any appearing among the ferric salts with the exception of ferric sulphocyanate. In thicker masses it is nearly or quite black; when melted and allowed to solidify, it forms a blackish red crystalline mass, which looks brown on a surface of fracture.* When the plates are examined under the polarizing microscope, they give evidence that they belong to one of the uniaxial systems, but the outlines of these crystals are so ragged that they furnish no means of deciding to which system they belong. Accordingly some of the plates immersed in ether, in which they dissolve very slowly, were observed under the microscope, when the formation of regular hexagonal holes was observed; there is no doubt, therefore, that the crystals belong to the hexagonal system. If the salt is resublimed slowly, it can be obtained in broad thin plates with a brilliant vitreous lustre; but on one occasion very small yellow plates were formed which called to mind the "gold filings" of Serullas. The melting point of the substance is given by Thomson as 177°; we have not attempted to determine this point anew, as it seemed to us of little practical value on account of the very deliquescent nature of the salt. If heated to about the fusing point of soft glass in an inert gas it sublimes essentially unaltered. When sublimed in a stream of nitrogen, part of the iodide is deposited in the red plates already described, the rest is carried on further in the tube as a yellowish cloud, which deposits a dark reddish brown amorphous powder; this is found to be much more susceptible to the action of atmospheric moisture than the red plates, but we think this difference in behavior is due only to the difference in the size of the particles in the two specimens. The sublimation may take place in nitrogen, carbonic dioxide, or even hydrogen, but oxygen must be carefully excluded, as this decomposes the iodide rapidly at not very high temperatures, so that on gently heating a sample of it in a porcelain crucible in a few minutes all the iodine has passed off in violet fumes, and there is left a reddish brown residue of ferric oxide, which retains the shape of the crystals of the ferrous iodide, and is magnetic. That this latter property was not due to the presence of some magnetic oxide or metallic iron in the residue was proved by dissolving it in hydrochloric acid, when a strong test for ferric chloride, but none whatever for ferrous chloride, was obtained. The iodine is so completely removed by this ignition in air that the process was used as a method of analyzing the ferrous iodide (Analyses IX. and X.). De Luca observed a similar decomposition of his (white) ferrous iodide. The same decomposition of the ferrous iodide by the oxygen of the air takes place slowly at ordinary temperatures; a specimen of it kept in a good desiccator gives off enough iodine vapor in time to color the air within the desiccator a distinct purple. A sample of the salt was kept in a desiccator over potassic hydrate, to absorb the iodine, for thirteen months, and the decomposition followed by occasional weighings, when it was found that about seven eighths of the total loss of iodine was given off in the first six months, but that even at the end of thirteen months the decomposition was not complete, as the residue still contained a little iodine, and gave tests for both ferrous and ferric compounds. It follows from these observations that the salt should not be allowed to stand even in a desiccator before analysis, but should be analyzed as soon as possible after its preparation.

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* The dark color of the ferrous iodide is not without analogy, as G. P. Baxter has found in this Laboratory that ferrous bromide has a dark yellow color with a greenish brown tinge.

If the salt is exposed to the atmosphere, it deliquesces quickly to a brown solution. The thinner plates, when kept in a corked flask or a desiccator, behaved in a very striking way; the red plate showed at first a white border around its edge, which gradually spread inward, until the whole plate became white; this change was soon followed by a liberation of iodine, which imparted a gray or even black appearance to the mass. The appearance of the iodine is undoubtedly due to the decomposition by air just described, but the cause of the whitening of the crystals was not so evident. The most obvious theories were, that the white substance was a second modification of the ferrous iodide, or that it was produced by the absorption of water, which might either form enough of the green ferrous iodide containing four molecules of water of crystallization to neutralize optically the red color of the anhydrous salt, or might give a definite compound containing less water of crystallization than the green salt.

The idea that the white substance was a second modification gained some support from the observations of Thomson, Carius and Wanklyn, and De Luca, who describe ferrous iodide as white or gray, and also from the fact that the white compound was formed in atmospheres containing very little water, although in none of these cases had moisture been rigorously excluded. We, therefore, tried a number of experiments to settle this point. In all of these it was necessary to select specimens of the salt which show this change from red to white, such as rather thin red plates or the brown amorphous powder obtained by sublimation, since thicker plates or masses of the iodide show the phenomenon with difficulty or not at all. We see no reason, however, to ascribe these differences in behavior to anything except the size of the crystals. Two similar portions of the ferrous iodide were exposed, the one to dry carbonic dioxide, the other to moist carbonic dioxide, the experiments being carried on at the same time and under parallel conditions. The specimen in the moist gas turned white quickly, while that in the dry gas remained unaltered. Other similar experiments showed that the change of color took place much more slowly in a gas containing little moisture than in one containing more. In all these experiments the amount of moisture must be kept small, as, if too much aqueous vapor is used, the salt deliquesces so rapidly that the formation of the white body cannot be observed. A sample of ferrous iodide was immersed in absolute ether (dried with sodium), and underwent no change of color even after long standing; when, however, a minute fraction of a drop of water was added, it rapidly turned white. Upon heating a specimen of the white body in a tube filled with dry carbonic dioxide a cloud appeared which looked like moisture and condensed in the cold part of the tube, the substance turning red at the same time. As the tube cooled this moisture was quickly reabsorbed, and the white body was formed again. This experiment was repeated several times with the same specimen. These experiments leave no doubt that the white substance is not a second isomeric modification of the ferrous iodide, but is formed by the action of water on the red anhydrous salt.

The question next arises, Is the white body a mixture of the red anhydrous and the green hydrous ferrous iodide, or is it a crystallized salt with a definite amount of water? Our experiments are not sufficiently conclusive to answer this question with certainty, but we would present the following argument in favor of the second view with all necessary reserve. A sample of ferrous iodide was exposed at ordinary temperatures (in this case about 22°) to an atmosphere of hydrogen kept moist by contact with dilute sulphuric acid containing 33 per cent of acid, and the absorption of water followed by successive weighings at intervals of about a day. Upon plotting these results a curve was obtained, which showed a change in the rate of absorption at a certain point, and a calculation of the amount of water absorbed at this point gave the following result:

0.4289 gram of ferrous iodide absorbed 0.0491 gram of water.

	Calculated for $FeI_2 2H_2O$.	Found.
Water	10.40	10.28

The coincidence of these numbers is certainly striking, and, so far as it goes, tells in favor of a definite composition for the white body; but little weight can be given to a single determination, and in this case the result must be regarded with the more suspicion, because the ferrous iodide, after it had turned from red to white in this experiment, became gray from decomposition with liberation of iodine.

When one of the red plates was viewed under the polarizing microscope in ordinary air, it appeared at first granular and then white, at the same time assuming a lower order of symmetry, as extinction was observed at certain angles when the stage was rotated, an effect which could not have been produced by the original crystal, as it was a hexagonal plate bounded by two basal planes. This observation shows little more than that the white substance was crystalline.

The anhydrous ferrous iodide dissolves rapidly and freely in water with a considerable evolution of heat. The dilute solutions are colorless, the stronger ones green. The hot saturated solutions deposit green crystals of $FeI_2 4H_2O$. Our analysis of this salt gave results which agreed only approximately with those required by the theory, but this is not strange, as it is very deliquescent and rapidly decomposed by the oxygen of the air with liberation of iodine. The water cannot be determined by loss, as the salt gives off hydriodic acid when it is heated. Fortunately it was not necessary for us to spend our time in attempting to obtain better analytical results, as Volkmann* has made a careful study of crystallized ferrous iodide, and has isolated it with four, six, or nine molecules of water of crystallization. From his description of the preparation of these salts there can be no question that the salt obtained by us was $FeI_2 4H_2O$.

The solution of ferrous iodide, when exposed to the air, is decomposed, turning at first brown and then throwing down a yellowish brown precipitate of ferric hydrate or a basic ferric salt; iodine is set free at the same time, and apparently some hydriodic acid is also formed.

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* Ber. d. chem. Ges. 1894, R. 618.

The ferrous iodide is very susceptible to the action of oxydizing agents, as appears from the account given above of the action of air on it at ordinary temperatures, but it shows a very striking resistance to the action of reducing agents. Its behavior in this respect was studied with some care in the hope of perhaps encountering a subiodide. As has been already stated, ferrous iodide can be sublimed essentially unaltered in an atmosphere of dry hydrogen. This is not perhaps altogether unexpected, as it has been found in this Laboratory that cobaltous bromide is only partially reduced when heated in dry hydrogen, the remainder subliming unaltered, while nickelous bromide was reduced under the same conditions essentially without sublimation.* When hydrogen was passed through melted ferrous iodide, no more reduction was obtained. Ferrous iodide sublimed through a layer of iron by hydrogen remained unaltered. Mercury alone or when emulsified by grinding with diatomaceous earth produced no effect on ferrous iodide even when distilled with it. When melted with molecular silver, on the other hand, the reduction to metallic iron was complete. Reductions in the moist way with hydriodic acid and iron by hydrogen or zinc dust also seemed to give negative results.

C. Liebermann and H. Sachse,† and also P. Bruck,‡ have recommended ferrous iodide as a useful carrier in adding iodine to derivatives of acetylene, such as phenylpropiolic acid, acetylenedicarboxylic acid, or propargylic acid. We have also tried some experiments on the behavior of ferrous iodide with organic compounds, but as the results are of little interest, we shall summarize them as briefly as possible. Ferrous iodide, when heated to redness in ethylene, was reduced, leaving a magnetic residue containing carbon. With acetylene a very gentle heat was sufficient to start a reaction, which afterward proceeded by itself accompanied by a dull red glow. The products were a volatile yellow liquid containing much iodine and a voluminous residue consisting of carbon and very little iron. The fact that the ferrous iodide is reduced by these hydrocarbons, when it is almost unaffected by hydrogen, is remarkable. Isopropyl alcohol heated with ferrous iodide gave a little of an insoluble oil, probably the iodide. When treated with an ethereal solution of aniline, the ferrous iodide formed a white compound much more voluminous than the original salt; this in all probability is an aniline addition product analogous to the ammonia compound described later. Benzol, benzylchloride, ether, phenol, or hydroquinone gave no perceptible action with ferrous iodide.

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* Richards and Baxter, These Proceedings, XXXIV. 352.

† Ber. d. chem. Ges., XXIV. 4112.

‡ Ibid. 4118.

OTHER METHODS OF PREPARING FERROUS IODIDE.

In this section of the paper we shall describe a revision of the methods used by our predecessors, and also some new methods of our own.

The revision of the older methods was necessary, because in three cases the ferrous iodide formed was described as gray or white; and although we have proved that the white samples formed from the red salt owed their change of color to absorption of water, it did not follow that those described by our predecessors were not anhydrous ferrous iodide in a second isomeric form. De Luca,* who states that ferrous iodide when pure is white, gives no method of preparation in any of the journals to which we have access, so that it was impossible for us to repeat his work. A. T. Thomson † prepared his gray ferrous iodide by evaporating an aqueous solution in a flask containing some free iron. On repeating this experiment we had so much difficulty from oxidation that we carried on our later attempts in an atmosphere of carbonic dioxide. Under these conditions, when the water of crystallization began to come off, the liquid became black and opaque-looking as if it contained a suspended black precipitate. Later the surface of the boiling mass became grayish white with a silvery lustre, but when all the water had been driven off, the residue was brownish red like the ferrous iodide prepared by our method. This experiment makes it probable that the gray ferrous iodide of Thomson owed its color to the presence of water, for in the absence of analyses he would undoubtedly have ascribed the brownish red color of the final residue to the formation of a ferric salt by oxidation.

As the method of Carius and Wanklyn ‡ consisted in heating iron and iodine in a porcelain crucible, it seemed at first sight that the gray color of the product could hardly be due to the presence of water, and therefore we repeated their work, following their directions as carefully as possible. One gram of rather coarse iron filings,§ mixed with a little iodine to drive out the air, was heated in a covered porcelain crucible to redness as quickly as possible; four grams of iodine were then added in two portions, and the heating continued until comparatively little iodine vapor escaped around the edges of the cover. When cool, the product was found to be a fused mass, consisting, after it had been broken out of the crucible, of red scales exactly like those described earlier in this paper. These scales upon exposure to the air soon turned grayish white, and then deliquesced to a brown solution. We have repeated this process of Carius and Wanklyn many times, and in every case the ferrous iodide formed has appeared in red scales, before it had been exposed to the air long enough to absorb moisture. We, therefore, are compelled to ascribe the gray color mentioned by Carius and Wanklyn to the absorption of water from the air, since they, like Thomson, would in the absence of analyses have supposed that the red color was due to oxidation. Our present knowledge, therefore, gives no reason for supposing that anhydrous ferrous iodide has any other color than red.

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* Comptes-Rendus, LV. 615.

† Gmelin-Kraut, Handbuch, III. 350, 6th edition.

‡ Ann. Chem., CXX. 69.

§ The success of the process depends on using filings of the right degree of coarseness. With too fine or too coarse filings unsatisfactory results are obtained.

Another method of preparation may be described here, as it was tried to see whether a white form might not be obtained at comparatively low temperatures. A small quantity of iron by hydrogen was placed in the middle of a small glass tube, and secured by two plugs of asbestos; an excess of iodine was inserted in one end of the tube, which was then filled with nitrogen and sealed at both ends. The end containing the iodine and iron was then heated to 120° by means of an air bath, and after most of the iodine had sublimed into the cold upper part of the tube, it was reversed so that this end and the iron were heated to 120°. After repeating this distillation of the iodine through the iron several times, all the metal was converted into the red ferrous iodide. This is a good method for preparing a specimen to be kept to show the color. Ferrous iodide was also made by passing hydrogen and iodine vapor over heated ferric oxide.

Of these methods of preparation, that of Carius and Wanklyn is the easiest, but it gives a product apt to be contaminated with metallic iron and oxide of iron. Thomson's method is tedious, and does not give a pure product, as we observed evolution of hydriodic acid toward the end of the evaporation even in an atmosphere of carbonic dioxide. The sealed tube method is also slow and imperfect, so that the best method, if the pure salt is desired, is the heating of iron and iodine in nitrogen given in the first part of this paper.

ACTION OF FERROUS IODIDE WITH AMMONIA.

When anhydrous ferrous iodide was exposed to a stream of ammonia gas at any temperature between 0° and 100°, a large amount of the gas was absorbed, and the iodide was converted into a voluminous white powder. The composition of this substance was determined by finding the increase in weight during the treatment with ammonia.

I. 3.5507 grams of ferrous iodide gained 1.1701 grams of ammonia.
II. 2.5411 grams gained 0.8449 gram of ammonia.

	Calculated for FeI_26NH_3.	Found. I.	II.
Ammonia	24.76	24.78	24.95

The substance therefore corresponds in formula to the compound $FeCl_2$-$6NH_3$ made from ferrous chloride under the same conditions.

PROPERTIES OF THE HEXAMMONIA FERROUS IODIDE.

It forms a pure white amorphous powder, which occupies many times the volume of the ferrous iodide from which it is made, and has a very low specific gravity. Water decomposes it at once with a considerable rise of temperature; the products are ferrous hydrate, ammonic iodide, and ammonia. We did not succeed in finding an organic solvent for it. When exposed to the air it gives off ammonia rapidly and turns brown; in an atmosphere of ammonia it remains unaltered even at 100°; heated in an indifferent gas it loses ammonia, and is converted into a dark brown powder, which seems to be stable in the air. Two analyses indicated that this brown substance contained between two and three molecules of ammonia to each molecule of ferrous iodide. Its stability in air leads us to think that it is a new compound, but evidently it was not pure, as the analyses differed by three per cent. Unfortunately we could find no way of purifying it.

ACTION OF BROMINE ON HEXAMMONIA FERROUS IODIDE.

When the compound FeI_26NH_3 was exposed to the vapor of bromine, it absorbed a large quantity, so that the product in one case contained 71.03 and in another 70.41 per cent of bromine. This apparent constancy in the amount of bromine absorbed led us to examine the product more carefully in the hope that it might be a definite compound, but our experiments have convinced us that it is only a mixture essentially made up of ferric bromide, ammonic bromide, and an ammonic bromiodobromide

NH_4BrIBr. The product had a reddish brown color, and gave off bromine when exposed to the air. It was investigated by treating it with ether, in which a portion dissolved with considerable evolution of heat. The residue insoluble in ether had a yellowish color, and seemed to be a mixture of ferric bromide and ammonic bromide in varying proportions. These two substances were recognized by the usual tests. The ether extract on evaporation left a residue which was green with a brilliant metallic lustre by reflected light, deep blood red by transmitted light; it resembled rosaniline, therefore, but the red color was less purplish than in that body. Examined with the microscope, crystals which looked like ammonic bromide were observed. It had a strong odor similar to that of bromide of iodine, and, although not really stable, could be kept for some time without much decomposition. Upon treating it again with ether a fresh quantity of the insoluble yellowish residue was left behind. The residue obtained by evaporating one of our first ether extracts was analyzed with the following results:

0.7149 gram of the substance gave 0.0216 gram of ferric oxide, 0.0405 gram of ammonia, 1.4289 grams of mixed silver salts which yielded 0.7652 gram of silver.

In calculating these results, as the iron from its small amount was evidently an impurity, the amount of ferric bromide corresponding to it has been subtracted from the amount of substance taken, and the bromine contained in this ferric bromide from the bromine found. As the substance gave a test for a ferrous salt, it would have perhaps been more correct to consider the iron present as ferroferric bromide, and this would have given numbers agreeing better with those calculated from the formula; but we think it wiser to give the results on the assumption that ferric bromide was present, as we cannot believe that the amount of ferrous bromide was more than a trace, since the substance had been exposed to an excess of bromine.

	Calculated for NH_4BrIBr.	Found.*
Ammonium	5.90	6.38
Iodine	41.64	40.96
Bromine	52.46	53.32

These numbers would seem conclusive if it were not for the presence of the small amount of ferric bromide (considered in calculating them) and the appearance under the microscope of crystals resembling ammonic bromide; but with these sources of error, we thought it necessary to support our analysis with evidence of some other sort, and therefore undertook the preparation of NH_4BrIBr direct in order to compare its properties with those of our compound. Upon treating ammonic bromide with an ethereal solution of bromide of iodine, the salt dissolved, giving a red solution, and on evaporation of the ether a residue was obtained the properties of which were identical with those of the ammonic bromiodobromide described above. Further, upon exposing ammonic iodide to the vapor of bromine an amount was absorbed corresponding very nearly to that required by the formula.

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* If the ferric bromide was not subtracted, the numbers were, NH_4 5.67, iodine 36.39, bromine 56.41.

1.6487 grams of ammonic iodide absorbed 1.7804 grams of bromine.

	Calculated for NH_4BrIBr.	Per cent of Bromine in the Product.
Bromine	52.46	51.92

During the action of the bromine the ammonic iodide at first turned black, but as the absorption went on it finally became scarlet, and this product proved to be identical with the ammonic bromiodobromide. A curve constructed from the increase of weight of the ammonic iodide showed that there was a marked diminution in the speed of the absorption after the first atom of bromine had been added. This decrease in the speed of absorption is undoubtedly connected with the conversion of the black substance into the red NH_4BrIBr, but we are unable to decide whether this black intermediate product is another compound NH_4BrI, or only a mixture of ammonic bromide and free iodine. It is a curious fact, in view of the absorption of free bromine by ammonic iodide, that, so far as we could find, an ethereal solution of bromine had no action on this salt. We have not continued our experiments in this direction for fear of intruding on the field of work occupied by Wheeler, who with Pratt and Barnes has prepared the ammonic triiodide.*

We have adopted provisionally the name ammonic bromiodobromide and the formula NH_4BrIBr for this substance, because it is made by the action of bromide of iodine on ammonic bromide, and when it decomposes bromide of iodine is given off and ammonic bromide left behind; but we do not feel that these observations settle its constitution finally, although they certainly are strong arguments in favor of the formula adopted. If this is correct, the formation from ammonic iodide and bromine must be preceded by the replacement of the iodine in the salt by bromine, and this may account for the fact noted above, that an ethereal solution of bromine does not act on ammonic iodide.

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* Am. Chem. Journ., XIX. 675 (1897).

PROPERTIES OF AMMONIC BROMIODOBROMIDE NH_4BrIBr.

The salt has a blood-red color in transmitted light, but is a brilliant green with a metallic lustre by reflected light. The specimens examined by us contained very elaborately twinned crystals with the branches at right angles, but we are inclined to think that these consisted of ammonic bromide, which is easily formed by the decomposition of our salt; on this account it smells of bromide of iodine, and on long standing leaves a white residue of ammonic bromide; the same decomposition takes place to a limited extent when it is dissolved in ether; the ethereal solution is dark red. When treated with water, bromine and iodine are set free, and a solution is formed. Hydrochloric acid sets free iodine. Sodic hydrate or ammonic hydrate gives a black precipitate of iodide of nitrogen; upon adding hydrochloric acid to the filtrate from this iodide of nitrogen, bromine is set free. Sulphurous acid gives hydrobromic acid and hydriodic acid.